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(54) **Stable liquid dishwashing detergent containing abrasive, clay and low density particles**

(57) Thixotropic liquid dishwashing detergents contain anionic surfactant, water-insoluble abrasive, colloidal clay suspending agent and water-insoluble low density particulate filler material. The compositions have a low yield value, yet exhibit phase stability due to the presence of the filler material.

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SPECIFICATION

Stable liquid dishwashing detergent containing abrasive, clay and low density particles

5 *Technical field*

The present invention relates to thixotropic liquid dishwashing detergents having a relatively low yield value and containing anionic surfactant, water-insoluble abrasive, colloidal clay suspending agent, and a water-insoluble low density particulate filler material to improve phase stability.

Abrasive-containing liquid detergents are useful for cleaning food soils, particularly burnt or dried-on foods, from kitchenware. Such compositions are highly effective at removing food soils when used undiluted or in the form of a concentrated aqueous slurry, and are acceptable for hand dishwashing in dilute aqueous solutions. These compositions typically contain a colloidal clay to help suspend the abrasive material. However, colloidal clays are not completely effective at suspending abrasives in liquid detergents having a relatively low yield value, which is desired for optimum dispensing and dispersion during use. This can result in some settling of abrasive and separation of a clear liquid layer at the top of the product over a period of time.

The present invention provides abrasive-containing liquid dishwashing detergents of relatively low yield value (i.e., from about 15 to about 50 dynes/cm²) having improved stability due to the presence of minor amounts of low density particulate filler material.

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Background art

U.S. Patent 4,457,856, Mitchell et al, issued July 3, 1984, discloses liquid dishwashing detergents containing anionic surfactant, suds stabilizing nonionic surfactant, water-insoluble abrasive and, preferably, a colloidal clay suspending agent. The compositions can have a yield value of from about 5 to about 600 dynes/cm².

U.S. Patent 3,985,668, Hartman, issued October 12, 1976, discloses liquid hard-surface cleaners containing abrasive, clay colloid-forming agent, and a particulate filler material, which preferably has a density of from about 0.2 to about 1.1. The filler improves stability by exerting an upward force on the structure of the colloid-forming agent to counteract the abrasive's tendency to compress the structure and squeeze out liquid.

U.S. Patent 3,615,972, Morehouse et al, issued October 26, 1971, discloses hollow thermoplastic microspheres useful for coatings, moldings and plastic smoke.

Summary of the invention

This invention relates to stable liquid dishwashing detergents comprising, by weight:

- (a) from about 15% to about 50% of an anionic surfactant;
- (b) from about 1% to about 15% of a water-insoluble abrasive having a particle diameter of from about 5 to about 250 microns and a hardness on the Mohs scale of from about 2 to about 8;
- (c) from about 0.1% to about 5% of a colloidal clay suspending agent;
- (d) from about 0.05% to about 3% of a water-insoluble particulate filler material having a diameter of from about 1 to about 250 microns and a density of from about 0.01 to about 0.5 g/cm³; and
- (e) from about 40% to about 75% of water;

said composition having a viscosity of from about 500 to about 2000 cps at 20°C and a yield value of from about 15 to about 50 dynes/cm².

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Detailed description of the invention

The present invention relates to thixotropic liquid dishwashing detergents containing anionic surfactant, water-insoluble abrasive, colloidal clay suspending agent, and water-insoluble low density particulate filler material. The compositions have a viscosity of from about 500 to about 2000, preferably from about 800 to about 1700, more preferably from about 1100 to about 1500, cps at 20°C. The compositions also have a yield value of from about 15 to about 50, preferably from about 25 to about 45, more preferably from about 30 to about 40, dynes/cm².

As used herein, yield value is determined as follows using an RTV Brookfield Viscometer with an LTV No 1 cylindrical spindle.

1. Fill a 16 oz. (0.476 l) glass jar, having an inside diameter of at least 7.6 cm, to the base of the neck with the product to be tested. Cap the jar and allow the sample to equilibrate for 2-5 days at 20°C.
2. Set the viscometer speed at 10 rpm. Adjust the 0-point on the dial to the extreme left side of the viscometer window.
3. Place the spindle in the sample to the depth indicated by the groove in the shaft. If the sample is extremely viscous, it may be necessary to move the jar back and forth until the sample fills in around the spindle.
4. Turn on the viscometer. When the needle has moved 1.25-2.5 cm across the window, depress the clutch and stop the viscometer.

5. After 2 minutes, release the clutch and observe the movement of the pointer. Record readings to the nearest 0.25 units every 15 seconds. When the difference between successive readings is equal to 0.5 units or less for three successive readings, or the difference has remained constant for a period of 1 minute or more, note the pointer reading. This should take 2 to 5 minutes.

6. Using the first reading where the difference between readings was 0.5 units or less, or the first reading where the difference became constant, a yield value is calculated as follows:

$$\text{Yield Value} = \text{reading} \times 1.72 \text{ dynes/cm}^2$$

As used herein, viscosity is determined as follows using an RTV Brookfield Viscometer with an RTV No. 5 spindle.

1. Fill a 16 oz. (0.476 l) glass jar, having an inside diameter of at least 7.6 cm, to the base of the neck with the product to be tested. Allow the sample to equilibrate to 20°C.
2. Place the spindle in the sample to the depth indicated by the groove in the shaft.
3. Set the viscometer speed to 50 rpm. Depress the clutch and turn on the viscometer. Release the clutch and allow the spindle and dial to rotate for two minutes. Then depress the clutch, stop the viscometer, and record the dial reading.

4. Repeat step 3 with the rpm setting at 100.

5. Viscosity is calculated as follows:

$$\text{Viscosity} = (\text{reading at 100 rpm} - \text{reading at 50 rpm}) \times 80 \text{ cps.}$$

- Despite their low yield values, the compositions herein exhibit acceptable phase stability due to the incorporation of the low density particulate filler material. It is believed that the filler material improves stability by lowering the specific gravity of the clay mass so that it floats in the liquid phase of the composition. The type and amount of the filler material should be selected such that the specific gravity of the final composition is adjusted to match that of the clear fluid (i.e., the composition without the clay and abrasive materials) so that little or no clear fluid separates during storage of the composition. Acceptable stability is obtained when a 650 ml bottle of the composition has less than 20 ml of clear fluid on the top and less than 100 ml of clear fluid on the bottom after storage for 6 months at ambient conditions. Preferably there is less than 10 ml of clear fluid on the top and less than 50 ml of clear fluid on the bottom. More preferably, there is less than 5 ml of clear fluid on the top and less than 20 ml of clear fluid on the bottom. Since the compositions can encounter elevated temperatures during storage, it is also preferred that the above limits be met when the compositions are stored for 2 weeks, and preferably for 4 weeks, at 50°C.

Anionic surfactant

The compositions of this invention contain from about 15% to about 50%, preferably from about 20% to about 35%, by weight of an anionic surfactant, or mixtures thereof.

Anionic surfactants can be broadly described as the water-soluble salts, preferably the alkali metal (especially sodium and potassium) salts, of organic sulfuric reaction products having in their molecular structure an alkyl radical containing from about 8 to about 22 carbon atoms and a radical selected from the group consisting of sulfonic acid and sulfuric acid ester radicals. Included in the term alkyl is the alkyl portion of acyl radicals.

Examples of anionic synthetic surfactants are alkyl sulfates, especially those obtained by sulfating the higher alcohols (C_8 - C_{18} carbon atoms); alkyl benzene or alkyl toluene sulfonates in which the alkyl group contains from about 9 to about 15 carbon atoms, the alkyl radical being either a straight or branched aliphatic chain; paraffin sulfonates and olefin sulfonates in which the alkyl or alkenyl group contains from about 10 to about 20 carbon atoms; alkyl glyceryl ether sulfonates, especially those ethers of the higher alcohols derived from tallow and coconut oil; coconut oil fatty acid monoglyceride sulfates and sulfonates; and condensation products of C_8 - C_{18} alcohols or C_8 - C_{12} alkyl phenol with from about 1 to about 30 moles of ethylene oxide per mole of alcohol or alkyl phenol.

Anionic surfactants useful herein are described in greater detail in U.S. Patent 4,457,856, Mitchell et al, issued July 3, 1984, incorporated herein by reference.

Particularly preferred anionic surfactants herein are alkyl ether sulfates having the formula $RO(C_2H_4O)_xSO_3M$, wherein R is alkyl or alkenyl of from about 10 to about 18, preferably from about 12 to about 16, carbon atoms, x is from 0 to about 12, preferably from about 1 to about 4, and M is a water-soluble cation.

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Optional surfactants

The compositions herein preferably also contain from about 1% to about 15%, more preferably from about 1.5% to about 8%, by weight of a suds stabilizing nonionic surfactant, or mixtures thereof. Suds stabilizing nonionic surfactants herein are of three basic types -ethylene oxide condensate, amides, and amine oxides.

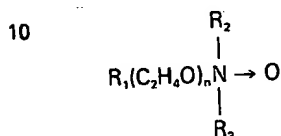
The ethylene oxide condensates are broadly defined as compounds produced by the condensation of ethylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound which can be aliphatic or alkyl aromatic in nature. The length of the hydrophilic or polyoxyalkylene radical which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements. Such ethylene ox-

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ide condensates are described in the above cited U.S. Patent 4,457,856, incorporated herein by reference.

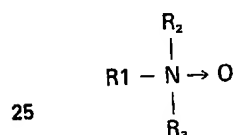
Preferred amide surfactants include the ammonia, monoethanol and diethanol amides of fatty acids having an acyl moiety of from about 8 to about 18 carbon atoms. These acyl moieties may be derived from naturally occurring glycerides, e.g., coconut oil, palm oil, soybean oil and tallow, or derived synthetically, e.g., by the oxidation of petroleum, or by hydrogenation of carbon monoxide by the Fischer-Tropsch process. The monoethanol amides and diethanolamides of C₁₂₋₁₄ fatty acids are preferred.

Preferred amine oxide semipolar nonionic surfactants comprise compounds and mixtures of compounds having the formula:



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wherein R₁ is an alkyl, 2-hydroxyalkyl, 3-hydroxyalkyl, or 3-alkoxy-2-hydroxypropyl radical in which the alkyl and alkoxy, respectively, contain from about 8 to about 18 carbon atoms, R₂ and R₃ are methyl, ethyl, propyl, isopropyl, 2-hydroxyethyl, 2-hydroxypropyl, or 3-hydroxy-propyl, and n is from 0 to about 10. Particularly preferred are amine oxides of the formula:



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wherein R₁ is a C₁₀₋₁₄ alkyl and R₂ and R₃ are methyl or ethyl.

The level and type of surfactants used in the compositions of this invention preferably provide an initial suds cover to a dishwashing solution and a suds cover after the washing of 8 plates when used at a concentration of 0.07% in 2 gallons of 46°C water containing 7 grains/gallon water hardness measured as CaCO₃, each plate carrying 4.0 ml of a triglyceride containing soil. Suds are generated by agitation and the suds cover and height measured. A dinner plate carrying the soil is washed successively with the introduction of 4.0 ml of soil each time. An essentially complete suds cover of the washing solution is more important than suds height, but, preferably, the suds cover after the washing of 8 plates is at least about 1/2 inch in height.

The sudsing characteristic of the compositions of the invention preferably provides the user of the product with an indication of cleaning potential in a dishwashing solution. Solids encountered in dishwashing act as suds depressants and the presence or absence of suds from the surface of a dishwashing solution is a convenient guide to product usage. Mixtures of anionic surfactants and nonionic surfactants, especially amides and amine oxide nonionic surfactants, are utilized in the compositions of the invention because of their high sudsing characteristics, their suds stability in the presence of food soils and their ability to indicate accurately an adequate level of product usage in the presence of soil.

The compositions of the invention may also contain other surfactants such as ampholytic, zwitterionic and cationic surfactants.

Ampholytic surfactants can be broadly described as derivatives of aliphatic amines which contain a long chain of about 8 to 18 carbon atoms and an anionic water-solubilizing group, e.g., carboxy, sulfo or sulfate. Examples of compounds falling within this definition are sodium-3-dodecylamino propane sulfonate, and dodecyl dimethylammonium hexanoate.

Zwitterionic surface active agents operable in the instant composition are broadly described as internally-neutralized derivatives of aliphatic quaternary ammonium and phosphonium and tertiary sulfonium compounds in which the aliphatic radical can be straight chain or branched, and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfo, sulfato, phosphato, or phosphono.

Cationic surfactants such as quaternary ammonium compounds can find optional use in the practice of the invention to the extent they are compatible with the other surfactants in the particular composition.

Abrasive

The compositions herein contain from about 1% to about 15%, preferably from about 3% to about 8%, by weight of a water-insoluble abrasive material having a particle diameter of from about 5 to about 250, preferably from about 20 to about 125, microns and a hardness on the Mohs scale from about 2 to about 8, preferably from about 4 to about 7. Included are materials such as agate, mica, calcite, garnet, quartz, kieselguhr, silica, marble, tripoli, flint, feldspar, emery, pumice, alumina, perlite, expanded perlite, volcanic ash, diatomaceous earth, amorphous silica from dehydrated silica gels, precipitated silica, plastics such as polystyrene and polyacrylates, and natural and synthetic aluminosilicates and mixtures thereof.

Suspending agent

The compositions of the present invention also contain from about 0.1% to about 5%, preferably from about 0.3% to about 3%, more preferably from about 0.5% to about 1.5%, by weight of a colloidal clay suspending agent.

5 These clay materials can be described as expandable layered clays i.e., aluminosilicates and magnesium silicates. The term "expandable" as used to describe the instant clays relates to the ability of the layered clay structure to be swollen, or expanded, on contact with water. Preferred clays herein are those materials classified geologically as smectites (or montmorillonoids) and attapulgites (or palygorskites).

10 The smectite clays used in the compositions herein are all commercially available. Such clays include, for example, montmorillonite (bentonite), volchonskoite, nontronite, beidellite, hectorite, saponite, saucconite and vermiculite. The clays herein are available under commercial names such as Thixogel No. 1 (clay found in a relatively thin vein in the Black Hills) and various trade names such as "Fooler Clay" and Gelwhite GP from Georgia Kaolin Company, Elizabeth, New Jersey (both montmorillonites); Volclay BC and Volclay No. 325, from American Colloid Company, Skokie, Illinois; Black Hills Bentonite BH 450, 15 from International Minerals and Chemicals; Veegum Pro and Veegum F, from R. T. Vanderbilt (both hectorites); Barasym NAS-100, Barasym NAH-100, Barasym SMM 200, and Barasym LIH-300, all synthetic hectorites and saponites marketed by Baroid Division, NL Industries, Inc.

Smectite clays are highly preferred for use in the present invention. Montmorillonite, hectorite and saponite are the preferred smectites. Gelwhite GP, Barasym NAS-100, Barasym NAH-100, and Veegum F 20 are the preferred montmorillonites, hectorites and saponites.

Like the smectites, attapulgite clays are commercially available. For example, such clays are marketed under the trade name Attagel, i.e., Attagel 40, Attagel 50 and Attagel 150 from Engelhard Minerals & Chemicals Corporation.

Clay materials obtained under the foregoing commercial trade names can comprise mixtures of the 25 various discrete mineral entities. Such mixtures of the minerals are suitable for use in the present compositions. In addition, natural clays sometimes consist of particles in which unit layers of different types of clay minerals are stacked together (interstratification). Such clays are called mixed layer clays, and these materials are also suitable for use herein.

The colloid-forming clay materials useful herein are described more fully in U.S. Patent 3,985,668, Hart- 30 man, issued October 12, 1976, incorporated herein by reference.

Low density particulate filler material

The compositions also contain from about 0.05% to about 3% by weight of a water-insoluble particulate filler material having a diameter of from about 1 to about 250 microns, preferably from about 10 to 35 about 125 microns, and a density of from about 0.01 to about 0.5 g/cm³. Preferred particles have a density of from about 0.02 to about 0.3 g/cm³ and are used at a level of from about 0.07% to about 1% by weight of the composition. Particularly preferred particles have a density of from about 0.03 to about 0.1 g/cm³ and represent from about 0.09% to about 0.3% by weight of the composition.

40 The particulate filler should be selected to maintain its integrity in the present compositions for periods up to at least six months. The particles thus should be insoluble in the compositions. The particles also preferably should be able to withstand shearing stress without rupturing or cracking in order to survive conditions typically encountered during processing of the present compositions.

Suitable particulate filler material includes the thermoplastic microspheres described in U.S. Patent 3,615,972, Morehouse et al, issued October 26, 1971, incorporated herein by reference, such as those 45 made using the polymers described from column 3, line 26 to column 4, line 8. Thermoplastic microspheres are also described in U.S. Patents 3,864,181 and 4,006,273, both to Wolinski et al, incorporated herein by reference. Particularly preferred are the ultra low density, resilient polyvinylidene chloride microspheres sold by Pierce & Stevens Chemical Corp. under the name Miralite. Miralite 177 microspheres have an average particle size of about 30 microns, a particle size distribution of from 10-60 microns, and 50 a density of about 0.036 g/cm³.

Other suitable filler materials herein are the glass microspheres and hollow glass microballoons, such as those sold by Emerson & Cumings, Inc. under the name Microballoons, by P-Q Corp. under the name Q-Cel, by Union Carbide as Phenolic Microballoons, and by 3M Company under the name Glass Bubbles.

These materials have a particle size ranging from about 10-200 microns and a density of from about 0.1 55 to about 0.4 g/cm³.

Water

60 The compositions of this invention contain from about 40% to about 75%, preferably from about 45% to about 60%, by weight of water.

Optional ingredients

The compositions of the present invention can also contain from about 1% to about 20%, preferably from about 5% to about 15%, by weight of detergency builders, either of the organic or inorganic types. Examples of such builders are found in U.S. Patent 4,457,856, Mitchell et al, issued July 3, 1984, incorpo- 65 rated herein by reference.

Alcohols, such as ethyl alcohol, and hydrotropes, such as sodium and potassium toluene sulfonate, sodium and potassium xylene sulfonate, trisodium sulfosuccinate and related compounds (as disclosed in U.S. Patent No. 3,915,903, incorporated herein by reference) and urea, can be utilized in the interests of achieving a desired product phase stability, viscosity, and yield value. Ethanol at a level of from about 5% to about 12% and potassium or sodium sulfosuccinate at a level of from about 2% to about 5% are particularly useful.

Detergent compositions herein can contain any of the usual adjuvants, diluents and additives, for example, perfumes, enzymes, dyes, antitarnishing agents, antimicrobial agents, and the like. Alkalinity sources and pH buffering agents such as alkali metal carbonates and bicarbonates, monoethanolamine, triethanolamine and alkali metal hydroxides can also be utilized to adjust pH within the preferred 6.5 to 9, and most preferred 7 to 8, range.

The following examples illustrate the compositions of the present invention.
All parts, percentages and ratios used herein are by weight unless otherwise specified.

Example I

	Component	Wt. %	
		A	B
20	Sodium coconutalkyl sulfate	4.9	4.9
	Sodium coconutalkyl ethoxy(1) sulfate	24.1	24.1
	Coconutalkyl dimethylamine oxide	2.8	2.8
	Ethanol	7.3	7.3
	Sodium sulfosuccinate	3.1	3.1
25	Celite 319 abrasive (silica, avg. dia. 42 μ , Mohs hardness 6-7)	5.0	5.0
	HPM-20 sodium bentonite clay	0.85	0.85
	Miralite 177 (avg. dia. 30 μ , density 0.036 g/cm ³)	0.1	---
30	Glass microspheres (avg. dia. 70 μ , density 0.15 g/cm ³)	---	0.5
	Water and minors	Balance to 100	

The above Composition A of the present invention was prepared by high-shear mixing of an aqueous premix of the clay and abrasive with an aqueous premix containing the balance of the components. Composition A was also prepared by adding the Miralite to the clay and abrasive premix, and by adding the Miralite after mixing the two premixes. Composition B of the invention was prepared by adding the glass microspheres to finished product made by mixing the two premixes.

Samples of Composition A having viscosities ranging from about 1200 to 1500, cps at 20°C and yield values ranging from about 20 to 50 dynes/cm² exhibited much better phase stability, as indicated by relatively little or no separation of clear fluid after storage for up to 4 weeks at temperatures from 20°C to 50°C, than similar compositions without Miralite 177. A sample of Composition B exhibited no separation of clear fluid when stored at 20°C for 2 weeks.

Other compositions of the present invention are obtained when, in the above compositions, the sulfosuccinate is replaced with sodium chloride; the amine oxide is replaced with coconutalkyl monoethanol amide; the anionic surfactant system is changed to 11.6% of the alkyl sulfate and 12.4% of an alkyl ethoxy(3)sulfate; the anionic surfactant system is replaced with 12.6% sodium C₁₄₋₁₆ alpha olefin sulfonate and 7.4% ammonium coconutalkyl sulfate; or the abrasive is replaced with calcium carbonate having an average particle size of about 10 microns and a Mohs hardness of about 3.

CLAIMS

1. A stable liquid dishwashing detergent composition comprising, by weight:
 - (a) from about 15% to about 50% of an anionic surfactant;
 - (b) from about 1% to about 15% of a water-insoluble abrasive having a particle diameter of from about 2 to about 8;
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 - (c) from about 0.1% to about 5% of a colloidal clay suspending agent;
 - (d) from about 0.05% to about 3% of a water-insoluble particulate filler material having a diameter of
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- 10 (e) from about 40% to about 75% of water;
said composition having a viscosity of from about 500 to about 2000 cps at 20°C and a yield value of
from about 15 to about 50 dynes/cm²
2. A composition according to Claim 1 comprising from about 0.3% to about 3% of the colloidal clay.
3. A composition according to Claim 2 wherein the colloidal clay is a smectite clay.
- 15 4. A composition according to Claim 1 comprising from about 0.07% to about 1% of the particulate
filler material, which has a density of from about 0.02 to about 0.3 g/cm³.
5. A composition according to Claim 4 comprising from about 0.09% to about 0.03% of the particulate
filler material, which has a density of from about 0.03 to about 0.1 g/cm³.
6. A composition according to Claim 1 having a viscosity of from about 800 to about 1700 cps at 20°C
20 and a yield value of from about 25 to about 45 dynes/cm².
7. A composition according to Claim 5 comprising from about 3% to about 8% of the water-insoluble
abrasive, which has a particle diameter of from about 20 to about 125 microns, and from about 0.5% to
about 1.5% of the colloidal clay, which is a smectite clay.
8. A composition according to Claim 7 comprising from about 20% to about 35% of the anionic sur-
25 factant and from about 45% to about 60% of water.
9. A composition according to Claim 8 further comprising from about 1.5% to about 8% by weight of
a suds stabilizing nonionic surfactant selected from the group consisting of amine oxides and amides.
10. A composition according to Claim 9 having a viscosity of from about 1100 to about 1500 cps at
20°C and a yield value of from about 30 to about 40 dynes/cm².

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